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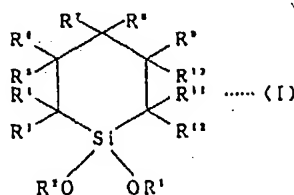
(54) [Title of the Invention] Organosilicon compounds, a catalyst for olefin polymerization, and a method of producing olefin polymers

(57) [Abstract]

[Problem] To offer an olefin polymerization catalyst which exhibits high activity and gives high stereo-regularity

[Resolution Means] An olefin polymerization catalyst which includes a solid catalyst component containing titanium, magnesium and an electron donor compound, an organoaluminium compound and an organosilicon compound represented by the following general formula (I).

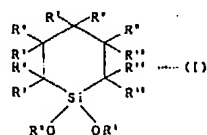
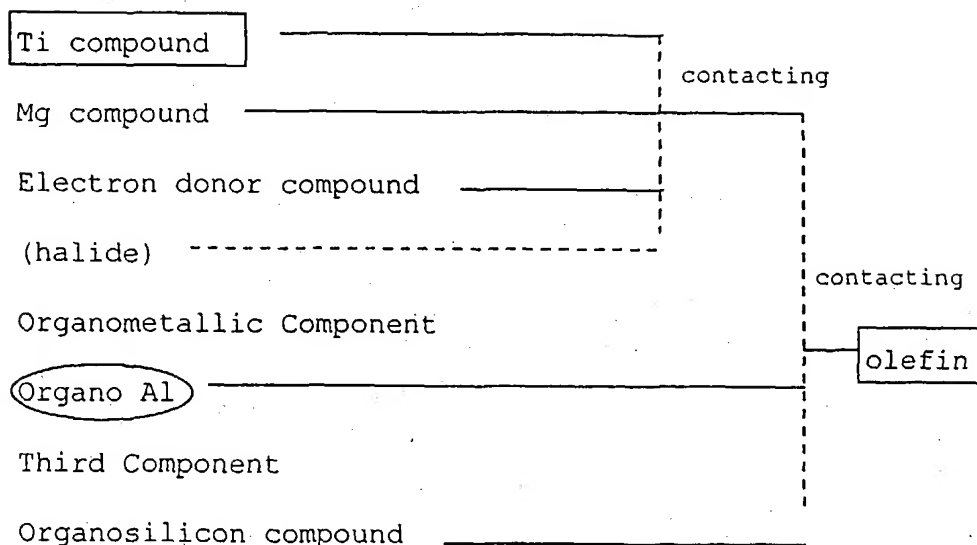
[Chem.1]



(In the formula, R^1 and R^2 represent an alkyl group with 1 to 20 carbons, R^3 and R^{12} represent a hydrocarbon group with 1 to 20 carbons, and R^4 to R^{11} represent a hydrogen atom or a hydrocarbon group with from 1 to 20 carbons.)

Figure 1

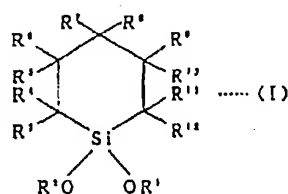
(A) Transition Metal Component



[Scope of Claims]

[Claim 1] Organosilicon compounds represented by the following general formula (I),

[Chem.1]



(where, R¹ and R² represent an alkyl group with 1 to 20 carbons and may be the same or different; R³ and R¹² represent a hydrocarbon group with 1 to 20 carbons and

may be the same or different, and they may also be coupled to an adjacent group to form a ring; and R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydrogen atom or a hydrocarbon group with 1 to 20 carbons and may be the same or different, and they may also be coupled to an adjacent group to form a ring).

[Claim 2] An olefin polymerization catalyst which is characterized in that it includes (A) a solid catalyst component containing titanium, magnesium and an electron donor compound, (B) an organoaluminium compound and (C) an organosilicon compound according to Claim 1.

[Claim 3] A method of producing olefin polymer which is characterized in that an olefin is polymerized using the olefin polymerization catalyst according to Claim 2.

[Claim 4] A method of producing olefin polymer according to Claim 3 where the olefin is propylene.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to organosilicon compounds, a catalyst for olefin polymerization and a method of producing olefin polymer; more specifically, it relates to a method in which there is employed an organosilicon compound of specified structure to produce an olefin polymerization catalyst which exhibits high activity and gives high stereoregularity, and to a method of producing olefin polymer.

[0002]

[Prior Art] Since they are crystalline macromolecules, olefin polymers, and in particular polypropylene, are excellent in terms of their stiffness, tensile strength, heat resistance, chemical resistance, optical properties and processability and, furthermore, they have a low specific gravity when compared to polystyrene and the like, so they are widely used in fields such as injection moulded articles of various kinds, containers and packaging materials, etc.

[0003] However, in order to broaden further the application fields of polypropylene, it is necessary to improve those of the above properties where polypropylene is inferior to polystyrene and ABS resin, namely stiffness and heat resistance. It is known that the stiffness and the heat resistance are raised as the stereoregularity of the polymer is increased, and so it is desirable to further enhance the stereoregularity.

[0004] Generally speaking, olefin polymers are produced by polymerization using a Ziegler Natta catalyst comprising a titanium compound and an organoaluminium compound, and efforts have been made to (1) enhance the catalyst activity, (2) improve the stereoregularity of the olefin polymer obtained, and (3) improve the polymer powder form for stable production, etc. As the catalyst for producing polypropylene, there is chiefly used a catalyst system consisting of a solid catalyst component comprising titanium, magnesium, chlorine and an electron donor compound, together with an organoaluminium

compound. It is also known that by adding an organosilicon compound with alkoxy groups to this catalyst system, the stereoregularity of the polymer produced may be raised. However, the stereoregularity and molecular weight distribution of the polypropylene produced by this catalyst system are not fully satisfactory.

[0005] Furthermore, methods have been reported using cyclic compounds as the organosilicon compound with alkoxy groups. For example, in JP-A-3-153709 there are proposed the compounds where, in aforesaid general formula (I), R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} are hydrogen atoms. Specifically, 1,1-dimethoxy-1-silacyclohexane is used but, by this method, the stereoregularity is insufficient. Again, in JP-A-9-110886 there are proposed compounds where at least one of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} in aforesaid general formula (I) is an alkyl group. Specifically, there are used 1,1-dimethoxy-1-silacyclopentane, 1,1-dimethoxy-2-ethyl-1-silacyclopentane, 1,1-dimethoxy-2,5-dimethyl-1-silacyclopentane, 1,1-dimethoxy-1-silacyclohexane and 1,1-dimethoxy-2-ethyl-1-silacyclohexane. However, by this method too, the stereoregularity is inadequate and the yield is low, so the method is impractical.

[0006] Consequently, these methods have not been altogether fully satisfactory in obtaining stereoregular polymer at high yields.

[0007]

[Problem to be Resolved by the Invention] The present invention has the objective of providing an olefin polymerization catalyst which exhibits high activity and which gives high stereoregularity, together with a method for producing olefin polymer.

[0008]

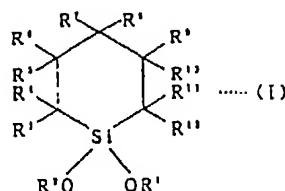
[Means for Resolving the Problem] As a result of painstaking research to achieve the aforesaid objective, the present inventors have discovered that, by using an olefin polymerization catalyst which includes a solid catalyst component containing titanium, magnesium and electron donor compound, an organoaluminium compound and an organosilicon compound represented by the following general formula (I), the aforesaid problem can be resolved, and the present invention has been perfected based on this discovery.

[0009] Specifically, the present invention offers the organosilicon compounds, the catalyst for olefin polymerization and the method of producing olefin polymer, shown below.

(1) Organosilicon compounds represented by the following general formula (I),

[0010]

[Chem.2]



[0011] (where R^1 and R^2 represent an alkyl group with 1 to 20 carbons and may be the same or different; R^3 and R^{12} represent a hydrocarbon group with from 1 to 20 carbons and may be the same or different, and they may also be coupled to an adjacent group to form a ring; and R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydrogen atom or a hydrocarbon group with from 1 to 20 carbons and may be the same or different, and they may also be coupled to an adjacent group to form a ring).

(2) An olefin polymerization catalyst which is characterized in that it contains a solid catalyst component (A) containing titanium, magnesium and an electron donor compound, (B) an organoaluminium compound and (C) an organosilicon compound as described in (1).

(3) A method of producing olefin polymer which is characterized in that an olefin is polymerized using olefin polymerization catalyst as described in (2).

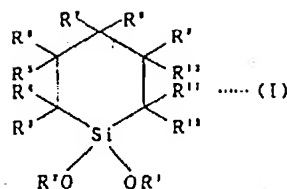
(4) A method of producing olefin polymer as described in (3) where the olefin is propylene.

[0012]

[Practical Embodiments of the Invention] The organosilicon compounds of the present invention are novel compounds of structure represented by aforesaid general formula (I). That is to say, they are organosilicon compounds represented by

[0013]

[Chem. 3]



[0014] (where R^1 and R^2 represent an alkyl group with 1 to 20 carbons and may be the same or different; R^3 and R^{12} represent a hydrocarbon group with 1 to 20 carbons and may be the same or different, and they may also be coupled to an adjacent group to form a ring; and R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} represent a hydrogen atom or a hydrocarbon group with from 1 to 20 carbons and may be the same or different, and they may also be coupled to an adjacent group to form a ring).

[0015] Specifically, examples of R^1 and R^2 are straight chain and branched alkyl groups such as the methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, pentyl group, hexyl group, octyl group and the like. Furthermore, R^1 and R^2 may be the same or they may be different. The methyl group is particularly preferred.

[0016] As examples of R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} , there are the hydrogen atom, straight chain hydrocarbon groups such as the methyl group and ethyl group, branched hydrocarbon groups such as the isopropyl group, isobutyl group, t-butyl group and texyl¹ group, saturated cyclic hydrocarbon groups such as the cyclobutyl group, cyclopentyl group and cyclohexyl group, and unsaturated cyclic hydrocarbon groups such as the phenyl group,

pentamethylphenyl group and the like. Furthermore, these groups may be the same or different. Of these, hydrogen, the methyl group and the ethyl group are preferred, with hydrogen particularly preferred.

[0017] As examples of R^3 and R^{12} , there are straight chain hydrocarbon groups such as the methyl group and ethyl group, branched hydrocarbon groups such as the isopropyl group, isobutyl group, t-butyl group and texyl group, saturated cyclic hydrocarbon groups such as the cyclobutyl group, cyclopentyl group and cyclohexyl group, and unsaturated cyclic hydrocarbon groups such as the phenyl group and pentamethylphenyl group. Furthermore, R^3 and R^{12} may be the same or different. Of these groups, the methyl group and ethyl group are preferred, in particular the methyl group.

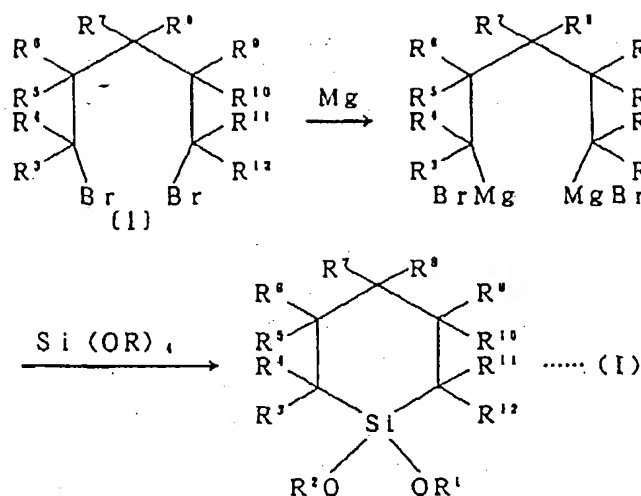
[0018] Furthermore, R^3 to R^{12} may form a ring by coupling with an adjacent group, such as in the case of 2-methyldecahydro-1-silanaphthalene or the like. Specific examples of preferred compounds are 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane, 1,1-dimethoxy-2,6-diethyl-1-silacyclohexane, 1,1-dimethoxy-2,6-diisopropyl-1-silacyclohexane, 1,1-dimethoxy-2,6-di-t-butyl-1-silacyclohexane, 1,1-dimethoxy-2,6-diphenyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-trimethyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-triethyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-triisopropyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-tri-t-butyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-triphenyl-1-silacyclohexane, 1,1-dimethoxy-2,6-diethyl-2-methyl-1-silacyclohexane, 1,1-dimethoxy-2,6-diisopropyl-2-methyl-1-silacyclohexane, 1,1-dimethoxy-2,6-di-t-butyl-2-methyl-

1-silacyclohexane, 1,1-dimethoxy-2,6-diphenyl-2-methyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6,6-tetramethyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6,6-tetraethyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6,6-tetraisopropyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6,6-tetra-t-butyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6,6-tetraphenyl-1-silacyclohexane, 1,1-dimethoxy-2,6-dimethyl-2,6-diethyl-1-silacyclohexane, 1,1-dimethoxy-2,6-dimethyl-2,6-diisopropyl-1-silacyclohexane, 1,1-dimethoxy-2,6-dimethyl-2,6-di-t-butyl-1-silacyclohexane, 1,1-dimethoxy-2,6-dimethyl-2,6-diphenyl-1-silacyclohexane and the like. As examples of especially preferred compounds, there are 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane, 1,1-dimethoxy-2,2,6-trimethyl-1-silacyclohexane and 1,1-dimethoxy-2,2,6,6-tetramethyl-1-silacyclohexane, with 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane being still further preferred.

[0019] The organosilicon compounds of the present invention can be synthesized by any method. A typical synthetic route is as follows.

[0020]

[Chem. 4]



[0021] In this synthetic route, the starting material compound [1] is either commercially available or can be obtained by known alkylation and/or halogenation, etc. By subjecting the compounds [1] to a known Grignard reaction, it is possible to obtain the organosilicon compounds represented by general formula (I). The olefin polymerization catalyst of the present invention is characterized in that it includes (A) solid catalyst component containing titanium, magnesium and an electron donor compound, (B) organoaluminium compound, and (C) organosilicon compound represented by the aforesaid general formula (I). Furthermore, the method of producing olefin polymer of the present invention is characterized in that the olefin is polymerized using the aforesaid olefin polymerization catalyst.

[0022] Below, the respective components, the method of preparation and the method of polymerization are explained.

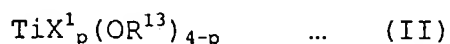
[I] The Individual Catalyst Components

(A) The solid catalyst component used for the olefin polymerization

The solid catalyst component for the olefin polymerization contains titanium, magnesium and an electron donor compound, and it is formed from the following titanium compound (a), magnesium compound (b), and electron donor compound (c).

(a) Titanium compound

As the titanium compound, there can be used a titanium compound represented by general formula (II).



[0023] In aforesaid general formula (II), X^1 represents a halogen atom, with a chlorine or bromine atom being preferred, and a chlorine atom being especially preferred. R^{13} is a hydrocarbon group, and this may be a saturated group or an unsaturated group which is linear or branched, or which may also be cyclic, and may possess a heteroatom such as sulphur, nitrogen, oxygen, silicon or phosphorus. Preferably, there is used a hydrocarbon group with from 1 to 10 carbons, in particular an alkyl group, alkenyl group, cycloalkenyl group, aryl group, aralkyl group or the like, with a straight chain or branched alkyl group being particularly preferred. In the case where a plurality of $-\text{OR}^{13}$ moieties are present, then these may be mutually the same or different. As specific examples of R^{13} , there are the methyl group,

ethyl group, n-propyl group, isopropyl group, n-butyl group, sec-butyl group, isobutyl group, pentyl group, hexyl group, heptyl group, octyl group, decyl group, allyl group, butenyl group, cyclopentyl group, cyclohexyl group, cyclohexenyl group, phenyl group, tolyl group, benzyl group and phenethyl group. 'p' denotes an integer in the range 0 to 4.

[0024] As specific examples of the titanium compounds represented by aforesaid general formula (II), there are the tetraalkoxytitaniums such as tetramethoxytitanium, tetraethoxytitanium, tetra-n-propoxytitanium, tetraiso-propoxytitanium, tetra-n-butoxytitanium, tetraiso-butoxytitanium, tetracyclohexyloxytitanium and tetraphenoxytitanium; titanium tetrahalides such as titanium tetrachloride, titanium tetrabromide and titanium tetraiodide; alkoxytitanium trihalides such as methoxytitanium trichloride, ethoxytitanium trichloride, propoxytitanium trichloride, n-butoxytitanium trichloride and ethoxytitanium tribromide; dialkoxytitanium dihalides such as dimethoxytitanium dichloride, diethoxytitanium dichloride, diisopropoxytitanium dichloride, di-n-propoxytitanium dichloride and diethoxytitanium dibromide; and trialkoxytitanium monohalides such as trimethoxytitanium chloride, triethoxytitanium chloride, triisopropoxytitanium chloride, tri-n-propoxytitanium chloride and tri-n-butoxytitanium chloride. Amongst these, the titanium compounds with a high halogen content are preferred, with titanium tetrachloride particularly preferred. These titanium compounds may each be used on their own, or they may be used in combinations of two or more types.

(b) Magnesium compound

As the magnesium compound, there can be employed a magnesium compound represented by general formula (III).



[0025] In aforesaid general formula (IV) (*sic*), R^{14} and R^{15} represent a hydrocarbon group, the group OR^{16} (where R^{16} is a hydrocarbon group) or a halogen atom. More specifically, the hydrocarbon group is a C_1 to C_{12} alkyl group, cycloalkyl group, aryl group or aralkyl group, R^{16} in the group OR^{16} represents a C_1 to C_{12} alkyl group, cycloalkyl group, aryl group or aralkyl group, and the halogen atom is chlorine, bromine, iodine or fluorine. Furthermore, R^{14} and R^{15} may be the same or different.

[0026] As specific examples of the magnesium compounds represented by aforesaid general formula (III), there are dimethylmagnesium, diethylmagnesium, diisopropylmagnesium, dibutylmagnesium, dihexylmagnesium, dioctylmagnesium, ethylbutylmagnesium, diphenylmagnesium, dicyclohexylmagnesium and other such alkyl- or aryl-magnesiums; dimethoxymagnesium, diethoxymagnesium, dipropoxymagnesium, dibutoxymagnesium, dihexyloxymagnesium, dioctyloxymagnesium, diphenoxymagnesium, dicyclohexyloxymagnesium and other such alkoxy- or aryloxy-magnesiums; ethylmagnesium chloride, butylmagnesium chloride, hexylmagnesium chloride, isopropylmagnesium chloride, isobutylmagnesium chloride, t-butylmagnesium chloride, phenylmagnesium bromide, benzylmagnesium chloride, ethylmagnesium bromide, butylmagnesium bromide, phenylmagnesium

chloride, butylmagnesium iodide and other such alkyl- or aryl-magnesium halides; butoxymagnesium chloride, cyclohexyloxymagnesium chloride, phenoxymagnesium chloride, ethoxymagnesium bromide, butoxymagnesium bromide, ethoxymagnesium iodide and other such alkoxy- or aryloxy-magnesium halides; magnesium chloride, magnesium bromide, magnesium iodide and other such magnesium halides.

[0027] Amongst these magnesium compounds, the magnesium halides, alkoxymagnesiums, alkylmagnesiums and alkylmagnesium halides can ideally be employed. The aforesaid magnesium compounds can be prepared from metal magnesium or compounds containing magnesium.

[0028] As an example, there is the method of effecting contact between metal magnesium, a halide and an alkoxy group-containing compound represented by general formula $X^2_m M(OR^{17})_{n-m}$ (where X^2 represents a hydrogen atom, halogen atom or hydrocarbon group with 1 to 20 carbons, M represents a boron, carbon, aluminium, silicon or phosphorus atom, and R^{17} represents a hydrocarbon group with from 1 to 20 carbons. n denotes the valency of M, and $n > m \geq 0$).

[0029] As examples of the aforesaid halides, there are silicon tetrachloride, silicon tetrabromide, tin tetrachloride, tin tetrabromide, hydrogen chloride and the like. Of these, silicon tetrachloride is preferred. As examples of the X^2 and R^{17} hydrocarbon groups, there are the methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, hexyl group, octyl group and other such alkyl groups, the

cyclohexyl group, the allyl group, propenyl group, butenyl group and other such alkenyl groups, the phenyl group, tolyl group, xylyl group and other such aryl groups, and the phenethyl group, 3-phenylpropyl group and other such aralkyl groups. Of these, the C_1 to C_{10} alkyl groups are particularly preferred. As a further example, there is the method of bringing a halide into contact with a magnesium alkoxide represented by $Mg(OR^{18})_2$ (where R^{18} represents a C_1 to C_{20} hydrocarbon group).

[0030] As examples of the halide here, there are silicon tetrachloride, silicon tetrabromide, tin tetrachloride, tin tetrabromide, hydrogen chloride and the like. Of these, silicon tetrachloride is preferred. As examples of R^{18} , there are the methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, hexyl group, octyl group and other such alkyl groups, the cyclohexyl group, the allyl group, propenyl group, butenyl group and other such alkenyl groups, the phenyl group, tolyl group, xylyl group and other such aryl groups, and the phenethyl group, 3-phenylpropyl group and other such aralkyl groups. Of these, the alkyl groups with from 1 to 10 carbons are particularly preferred.

[0031] These Mg compounds can be used on their own or they can be used supported on a carrier such as silica, alumina, polystyrene or the like, and moreover they can be used in combinations of two or more types. Furthermore, they can be used in the form of a mixture with a halogen or the like.

(c) Electron donor compound

As examples of the electron donor compound, there are oxygen-containing electron donor compounds such as alcohols, phenols, ketones, aldehydes, carboxylic acids, malonic acid, organic acid and inorganic acid esters, and ethers such as monoethers, diethers and polyethers, and also nitrogen-containing electron donor compounds such as ammonia, amines, nitriles, isocyanates and the like. Of these, the esters of polycarboxylic acids are preferred, with the esters of aromatic polycarboxylic acids further preferred. The esters of aromatic dicarboxylic acids are particularly preferred. Again, it is preferred that the organic group in the ester moiety be a straight chain, branched or cyclic aliphatic hydrocarbon.

[0032] Specific examples are the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1-ethylbutyl, 2-ethylbutyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, n-nonyl, 2-methylhexyl, 3-methylhexyl, 4-methylhexyl, 2-ethylhexyl, 3-ethylhexyl, 4-ethylhexyl, 2-methylpentyl, 3-methylpentyl, 2-ethylpentyl, 3-ethylpentyl and other such dialkyl esters of phthalic acid, naphthalene-1,2-dicarboxylic acid, naphthalene-2,3-dicarboxylic acid, 5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylic acid, 5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylic acid, indane-4,5-dicarboxylic acid, indane-5,6-dicarboxylic acid and other such dicarboxylic acids. Of these, the phthalic acid diesters are preferred, and it is also preferred that the organic group in the ester moiety be a straight chain or branched aliphatic hydrocarbon with at least 4 carbons.

[0033] As specific examples, there are di-n-butyl phthalate, diisobutyl phthalate, di-n-heptyl phthalate, diethyl phthalate and the like. Furthermore, these compounds may be used on their own, or two or more may be used in combination.

(B) The organoaluminium compound

As the organoaluminium compound (B) employed in the present invention, there can be used aluminium compounds containing an alkyl group, halogen atom, hydrogen atom or alkoxy group, or aluminoxanes, or mixtures thereof. Specific examples are trimethylaluminium, triethylaluminium, triisopropylaluminium, triisobutylaluminium, trioctylaluminium and other such trialkylaluminiums; diethylaluminium monochloride, diisopropylaluminium monochloride, diisobutylaluminium monochloride, dioctylaluminium monochloride and other such dialkylaluminium monochlorides; ethylaluminium sesquichloride and other such alkylaluminium sesquichlorides; and methyl aluminoxane and other such chain-form aluminoxanes. Amongst these organoaluminium compounds, the trialkylaluminiums with C₁ to C₅ lower alkyl groups, and in particular trimethylaluminium, triethylaluminium, tripropylaluminium and triisobutylaluminium, are preferred. Again, these organoaluminium compounds can be used on their own or two or more types may be used in combination.

(C) The organosilicon compounds

In the olefin polymerization catalyst relating to the present invention, there is used an organosilicon compound (C) represented by aforesaid general formula (I).

[0034] Such organosilicon compounds may be used on their own or two or more types may be employed in combination. The amount of the organosilicon compound (C) will be a molar ratio in the range from 0.001 to 5, and preferably 0.01 to 1, in terms of the organoaluminium compound (B).

[II] Preparation of the Solid Catalyst Component

The preparation of aforesaid solid catalyst component (A) may be carried out by effecting contact, by a normal method, between aforesaid titanium compound (a), magnesium compound (b), electron donor compound (c) and, optionally, a halide (d) such as silicon tetrachloride.

[0035] As examples of such known methods, there are the methods described in JP-A-53-43094, JP-A-55-135102, JP-A-55-135103 and JP-A-56-18606. For example, the solid catalyst component can be prepared by (1) the method of pulverizing the magnesium compound or a complex of the magnesium compound and the electron donor compound in the presence of the electron donor compound and, optionally, a pulverizing auxiliary, or the like, and then reacting with the titanium compound; (2) the method of reacting a liquid-form magnesium compound having no reduction capacity and a liquid titanium compound in the presence of the electron donor compound, and bringing about precipitation of the solid titanium complex; (3) the method of performing reaction between a titanium compound

and material obtained in (1) or (2) above; (4) the method of bringing about further reaction between an electron donor compound and titanium compound together with the material obtained in (1) or (2) above; and (5) the method in which the magnesium compound or a complex of the magnesium compound and the electron donor compound is pulverized in the presence of electron donor compound, titanium compound and, optionally, pulverizing auxiliary, or the like, after which treatment is carried out with a halogen or halogen compound.

[0036] Furthermore, as well as these, it is also possible to prepare the aforesaid solid catalyst component (A) by the methods described in JP-A-56-166205, JP-A-57-63309, JP-A-57-190004, JP-A-57-300407 and JP-A-58-47003, etc. Moreover, it is possible to prepare the solid catalyst component by effecting contact between the solid formed by supporting the aforesaid magnesium compound on an oxide of an element belonging to Groups II-IV of the Periodic Table, for example an oxide such as silicon oxide or magnesium oxide, or a composite containing at least one type of such oxide of an element belonging to Groups II-IV of the Periodic Table, for example silica alumina or the like, and the electron donor compound plus the titanium compound, in a solvent at a temperature in the range 0 to 200°C, preferably 10 to 150°C, for from 2 minutes to 24 hours.

[0037] The amount of the aforesaid titanium compound used should normally be from 0.5 to 100 mol, and preferably from 1 to 50 mol, per 1 mol of magnesium in the aforesaid magnesium compound. Again, the amount of the aforesaid electron donor compound used should

normally be from 0.01 to 10 mol, and preferably from 0.05 to 0.30 mol, per 1 mol of magnesium in the aforesaid magnesium compound. Furthermore, silicon tetrachloride may be added as the halogen compound.

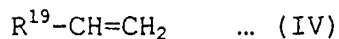
[0038] The contacting temperature should normally be from -20 to 200°C, preferably from 20 to 150°C, and the contacting time is normally in the range from 1 minute to 24 hours, preferably from 10 minutes to 6 hours. The contacting procedure is not particularly important. For example, each component may be brought into contact in the presence of an inert solvent such as a hydrocarbon, or each component may be diluted beforehand with an inert solvent such as a hydrocarbon and then contact effected. As examples of the inert solvent, there are aliphatic hydrocarbons such as n-pentane, isopentane, n-hexane, n-heptane, n-octane, isooctane and the like; and aromatic hydrocarbons such as benzene, toluene, xylene and the like.

[0039] Furthermore, the contacting with the titanium compound should be carried out two or more times, to fully bring about the supporting thereof on the magnesium compound which has the role of a catalyst support. The solid catalyst component obtained by effecting contact as described above may then be washed with an inert solvent such as a hydrocarbon. This inert solvent should be the same as described above. Moreover, the solid product obtained can be kept in the dry state or it can be kept in an inert solvent such as a hydrocarbon.

[III] Polymerization

With regard to the amounts of the respective catalyst components used in the present invention, there is employed an amount of the solid catalyst component, i.e. component (A), such that by conversion to titanium atoms there is normally from 0.0005 to 1 mmol thereof present per litre of reactor volume, and there is used an amount of the organoaluminium component, i.e. component (B), such that the atomic ratio of aluminium/titanium is normally from 1 to 1000, and preferably from 10 to 500. Outside of this range of atomic ratios, the catalyst activity will be inadequate. Again, there is used an amount of organosilicon compound, i.e. component (C), such that the molar ratio of organosilicon compound (C)/organoaluminium compound (B) is normally in the range from 0.02 to 2.0, and preferably 0.05 to 1.0. If the molar ratio lies outside of this range, then sufficient catalytic activity is not obtained.

[0040] The olefin employed in the present invention is preferably an α -olefin represented by general formula (IV).



In general formula (IV), R^{19} is a hydrogen atom or a hydrocarbon group, and the hydrocarbon group may be saturated or unsaturated, linear or branched, or it may also be cyclic. Specific examples of the olefin are ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 3-methyl-1-pentene, 4-methyl-1-pentene, vinylcyclohexane and the like. These

olefins may be used on their own or two or more types may be used in combination.

[0041] Amongst the aforesaid olefins, propylene is especially suitable. Furthermore, the polymerization may be homopolymerization of the propylene alone or copolymerization with an α -olefin such as ethylene, 1-butene, 1-hexene or the like. Furthermore, there can also be used dienes such as butadiene, or various other types of olefin. In the polymerization of the olefin in the present invention, where desired a preliminary polymerization of the olefin may firstly be carried out, after which the main polymerization is performed. In such circumstances, olefin is subjected to preliminary polymerization normally at a temperature in the range 1 to 100°C, at a pressure ranging from normal up to about 50 kg/cm²G, in the presence of catalyst formed by mixing aforesaid solid catalyst component (A), organoaluminium compound (B) and organosilicon compound (C) in the specified proportions, and then the main polymerization of the olefin is carried out in the presence of catalyst and the pre-polymerized product. The polymerization mode in the main polymerization is not especially restricted, and there may be employed solution polymerization, slurry polymerization, gas phase polymerization, bulk polymerization or the like. Slurry polymerization is particularly preferred. Furthermore, it is possible to employ either batch polymerization or continuous polymerization, or two-stage polymerization with different conditions in each, or block polymerization may be carried out using an α -olefin such as ethylene, 1-

butene or 1-hexene in the second stage. Furthermore, multistage polymerization may be employed.

[0042] Moreover, with regard to the reaction conditions, the polymerization pressure is not particularly restricted and it normally lies in the range from atmospheric to 80 kg/cm²G, preferably 2 to 50 kg/cm²G, while the polymerization temperature is normally suitably selected from within the range 20 to 90°C, and preferably 40 to 90°C. The polymerization time is governed by the type of raw material olefin and the polymerization temperature and so cannot be precisely stipulated but, normally, it is from 5 minutes to 20 hours, and preferably from 10 minutes to 10 hours.

[0043] The molecular weight can be adjusted by the addition of a chain transfer agent, preferably by adding hydrogen. Furthermore, nitrogen or other inert gas may also be present. Again, with regard to the catalyst components in the present invention, the olefin may be introduced and the reaction carried out immediately after mixing together the (A) component, (B) component and (C) component in the specified proportions and effecting contact therebetween, or, following such contacting, ageing may be carried out for about 0.2 to 3 hours, and then the olefin introduced and polymerization carried out. Furthermore, the catalyst components can be supplied suspended in an inert solvent or in the olefin, etc.

[0044] In the present invention, post-treatment following the polymerization can be carried out by the usual methods. That is to say, in the gas phase

polymerization method, following the polymerization, in order to eliminate olefin contained in the polymer powder withdrawn from the reactor, a current of nitrogen or the like may be passed through. Again, where required pelletization may be carried out by means of an extruder, and in order to bring about complete deactivation of the catalyst in such circumstances a small amount of water, alcohol or the like may be added. Furthermore, in the bulk polymerization method, following the polymerization, after completely separating-off monomer from the polymer removed from the polymerization reactor, pelletization can be carried out.

[0045]

[Examples] Next, the present invention is described in specific terms by means of examples but the invention is not to be restricted to the examples given. Now, the intrinsic viscosity $[\eta]$, the stereoregularity [mmmm], and the ratio of M_w/M_n were determined as follows.

Intrinsic viscosity $[\eta]$: Measured at 135°C dissolved in decalin.

Stereoregularity [mmmm]: Polymer was dissolved in 1,2,4-trichlorobenzene and then, using ^{13}C -NMR (EX-400 produced by JEOL Ltd.), quantitative determination was carried out employing the methyl group signals measured by the proton total decoupling method at 130°C.

[0046] The isotactic pentad percentage [mmmm] used in this invention denotes the percentage isotactic units amongst the pentad units in the polypropylene molecular

chain measured from the ^{13}C -NMR spectrum, as proposed by A. Zambelli *et al* in "Macromolecules, 6, 925, (1973)". Furthermore, the peak assignment determination method in this ^{13}C -NMR spectrum measurement was in accordance with that proposed by A. Zambelli *et al* "Macromolecules, 8, 687, (1975)".

Mw/Mn: This was calculated based on gel permeation chromatography (GPC) measurement results. Using 240 μl of a 1,2,4-trichlorobenzene (containing 300 ppm of BHT) solution of polymer concentration 0.1 wt/vol%, and employing a mixed polystyrene gel column (GMH6HT produced by Tosoh), measurement was conducted at 145°C at a flow rate of 1.0 ml/min. For detection, an infrared detector was used, and a wavelength of 3.41 μl was employed.

[Example 1] Synthesis of 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane

473.9 mg (19.5 mmol) of metal magnesium and 19.5 ml of diethyl ether were added to a 100 ml three-necked flask, then a few drops of 1,2-dibromoethane added, after which 2 g (7.8 mmol) of 2,6-dibromoheptane was added dropwise over 50 minutes. After refluxing and ageing for a further 8 hours, the disappearance of the starting materials was confirmed. After returning to room temperature, 1.19 g (7.8 mmol) of tetramethoxysilane was added dropwise, and then refluxing carried out for 14 hours. The consumption of the starting material was confirmed. Next, 5 ml of methanol was added, after which the solution was filtered and dried. By further distillation and column separation, 190 mg of 1,1-

dimethoxy-2,6-dimethyl-1-silacyclohexane was obtained at a purity of 97.5%. The yield was 12.8%.

[0047] Figure 2 shows the ^1H -NMR measurement results for the organosilicon compound using CDCl_3 as the solvent.

[Example 2]

(1) Preparation of the solid catalyst component

16 g (0.14 mol) of diethoxymagnesium was introduced into a stirred three-necked flask of internal capacity 500 ml which had been purged with nitrogen, and then 60 ml of dried heptane also added. After heating to 40°C , 2.45 ml (22.5 mmol) of silicon tetrachloride was added, then stirring carried out for 20 minutes and 12.7 mmol of dibutyl phthalate added. The solution was heated to 80°C and then 77 ml (0.70 mol) of titanium tetrachloride added using a dropping funnel. The internal temperature was made 110°C and stirring carried out for 2 hours so that the supporting of the titanium component was achieved. Subsequently, thorough washing was carried out using dry heptane. A further 122 ml (1.12 mol) of titanium tetrachloride was then added and, with the internal temperature at 110°C , stirring was carried out for 2 hours and a second Ti supporting process conducted. Thereafter, thorough washing was carried out using dry heptane.

(2) Propylene slurry polymerization

A stirred stainless steel autoclave of internal capacity 1 litre was thoroughly dried and purged with nitrogen,

after which 400 ml of dried heptane was added. Furthermore, 0.5 mmol of triethylaluminium and then 0.25 mmol of 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane were added. Next, there was added 0.005 mmol (in terms of the Ti) of the solid catalyst component prepared in (1), and 1.0 kg/cm²G of hydrogen and then the propylene introduced. With the autoclave at 80°C and at an overall pressure of 8.0 kg/cm²G, polymerization was carried out for 1 hour at a temperature of 80°C. Thereafter, the temperature was lowered, the pressure released and the contents extracted. After pouring into 2 litres of methanol, drying was carried out under vacuum and the polypropylene obtained. The results are shown in Table 1.

[Comparative Example 1]

(1) Preparation of the solid catalyst component

This was carried out in the same way as the preparation of the solid catalyst component in Example 2(1).

(2) Propylene slurry polymerization

This was carried out in the same way as in Example 2(2) excepting that 1,1-dimethoxy-2-ethyl-1-silacyclohexane was added instead of the 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane.

[Comparative Example 2]

(1) Preparation of the solid catalyst component

This was carried out in the same way as the preparation of the solid catalyst component in Example 2(1).

(2) Propylene slurry polymerization

This was carried out in the same way as in Example 2(2) excepting that 1,1-dimethoxy-1-silacyclohexane was added instead of the 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane.

[Example 3]

(1) Preparation of the solid catalyst component

13.3 g (0.14 mol) of magnesium chloride (anhydrous), 70 ml of decane and 65.5 ml (0.42 mol) of 2-ethylhexyl alcohol were introduced into a stirred three-necked flask of internal capacity 500 ml which had been purged with nitrogen, and then heating and reaction were carried out for 2 hours at 130°C to produce a uniform solution. Subsequently, 3.12 g (0.021 mol) of phthalic anhydride was added to this solution and further stirring carried out for 1 hour at 130°C, to bring about dissolution of the phthalic anhydride in the aforesaid uniform solution.

[0048] After cooling the uniform solution thus obtained to room temperature, the total quantity thereof was added dropwise over 1 hour into 373 ml (3.36 mol) of titanium tetrachloride which was held at -20°C. After the dropwise addition, the temperature of the uniform solution obtained was raised to 110°C over 4 hours and, on reaching 110°C, 5.39 ml (0.035 mol) of diisobutyl phthalate was added, following which stirring was carried out for 2 hours while holding at 110°C.

[0049] After completion of the 2 hours reaction, hot filtration was carried out and the solid material collected. This solid was re-suspended in 275 ml of titanium tetrachloride, following which heating and reaction were again carried out for 2 hours at 110°C. After the end of the reaction, hot filtration was performed once again and the solid collected. This was washed using 110°C decane and hexane. The washing was continued until no titanium compound could be detected in the washings, and the solid component was thus obtained.

(2) Propylene slurry polymerization

This was carried out by the same method as the propylene slurry polymerization in Example 2(2).

[Comparative Example 3]

(1) Preparation of the solid catalyst component

This was carried out by the same method as the preparation of the solid catalyst component in Example 3(1).

(2) Propylene slurry polymerization

This was carried out in the same way as in Example 2(2) except that 1,1-dimethoxy-2-ethyl-1-silacyclohexane was added instead of the 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane.

[Comparative Example 4]

(1) Preparation of the solid catalyst component

This was carried out in the same way as the preparation of the solid catalyst component in Example 3(1).

(2) Propylene slurry polymerization

This was carried out in the same way as in Example 2(2) excepting that 1,1-dimethoxy-1-silacyclohexane was added instead of the 1,1-dimethoxy-2,6-dimethyl-1-silacyclohexane.

[0050]

[Table 1]

Table 1

	Catalyst Activity (kg-PP/g-Ti)	$[\eta]$ (dl/g)	$[\text{mmmm}]$ (%)	Mw/Mn
Example 2	534	1.20	98.8	5.19
Comp.Ex. 1	334	0.92	96.9	5.05
Comp.Ex. 2	270	0.90	96.6	4.90
Example 3	500	1.14	98.8	5.30
Comp.Ex. 3	305	0.90	96.9	5.20
Comp.Ex. 4	255	0.89	96.8	5.15

[0051]

[Effects of the Invention] In accordance with the present invention, by using an organosilicon compound of specified structure, there is provided an olefin polymerization catalyst which exhibits high activity and gives high stereoregularity, together with a method of producing olefin polymer.

[Brief Explanation of the Drawings]

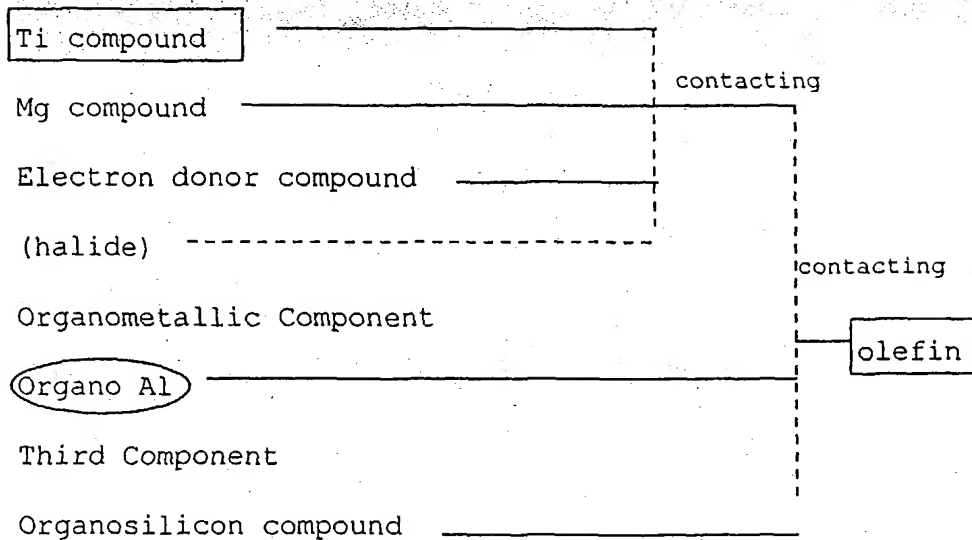
[Figure 1] Figure 1 is a flow chart showing a mode in the olefin polymerization of the present invention.

[Figure 2] Figure 2 is the ^1H -NMR chart (CDCl_3 solvent) of the organosilicon compound obtained in Example 1.

[Figure 1]

Figure 1

(A) Transition Metal Component

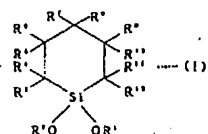


(B) Organometallic Component

Organo Al

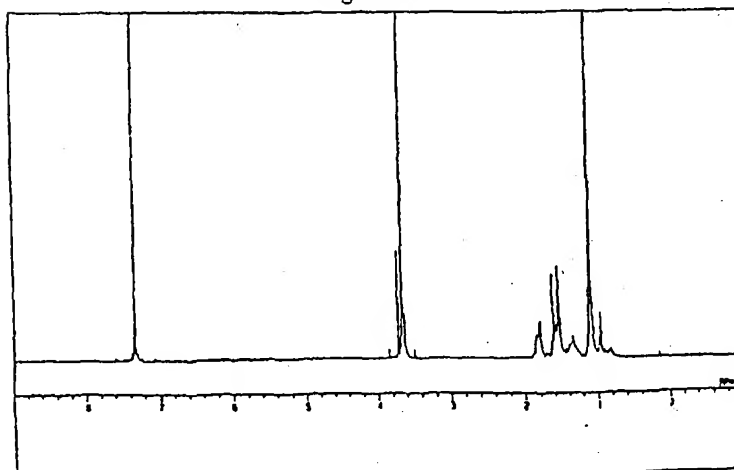
(C) Third Component

Organosilicon compound



[Figure 2]

Figure 2



¹ Translator's Note: The Japanese text here gives 'tekishiru' which would seem to be a transcription of "texyl". It is not clear whether this is an abbreviation (t-hexyl?) or a misprint.